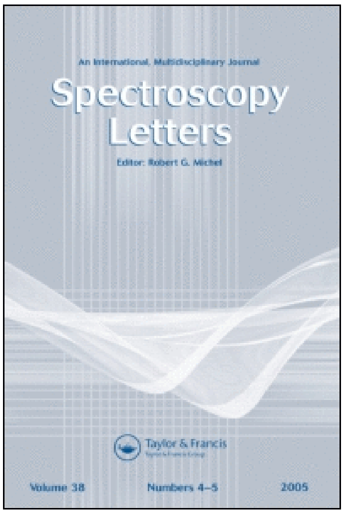

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Measurement and Interpretation of Ethanol ^{13}C Chemical Shifts Variations in Different Organic Solvents - Comparison with Aqueous Solvent

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MEASUREMENT AND INTERPRETATION OF ETHANOL ^{13}C CHEMICAL SHIFTS VARIATIONS IN DIFFERENT ORGANIC SOLVENTS - COMPARISON WITH AQUEOUS SOLVENT

Keywords : ^{13}C NMR, Hydrogen bond, ethanol, solvent effects

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ABSTRACT

The carbon chemical shifts of ethanol are measured in varied aqueous and organic solvents. We determine the hydrogen bonding effect between alcohol and bases by correcting the experimental values from anisotropy and non specific medium effects.

We prove that hydrogen bonding between hydroxylic hydrogen and bases lead to a shielding of C-α carbon and a very small effect on C-β carbon.

INTRODUCTION

^{13}C NMR spectroscopy can provide important informations regarding the conformations of the substituents for carbohydrates and recently (1,2), it has been proposed an assignment of the spectra by comparing ^{13}C chemical shifts in water to those in DMSO. However only few studies (2-4) concern such solvent effects. Values directly derived from measuring migration of the signals from the aqueous to the non aqueous solvents do not allow for interpreting these shifts in term of intramolecular hydrogen bonding. Indeed such values cannot be attributed only to complexation effects since various other mechanisms (non specific medium effects, magnetic anisotropy from the base, bulk susceptibility effects, ...) are not explicitely taken into account.

In recent studies (5-9) we proposed that ^{13}C shifts, measured from internal reference and corrected from anisotropy and non specific medium effects, can constitute very sensitive and discriminating parameters for complexation studies.

The present work is devoted to a ^{13}C study of association of ethanol with n or π bases with in mind a particular interest for the shifts between aqueous and non aqueous solvent. Ethanol was selected as proton donor so as to get simultaneous informations about CH_2 and CH_3 carbon behaviour in the association process.

EXPERIMENTAL

All spectra were recorded on a Bruker AM 300 spectrometer operating at 75.4 MHz. The magnetic field was locked on the ^{2}D signal of D_2O contained in a cylindrical cell inserted in the sample tube. The chemical shifts were measured from internal TMS (10 µl in 200 µl solution) and expressed in ppm, (positive values corresponding to downfield shifts). The probe temperature was 298° K. Spectra were sampled in a 64 K memory block (digital resolution 0.9 Hz) for a 29500 Hz spectral width, under complete ^1H noise decoupling mode with composite pulse decoupling. Scan number was adjusted to obtain a suitable signal noise ratio and a 2Hz exponential correction was made. Ethanol and the various bases were of spectroscopic grade and used without further purification.

RESULT AND DISCUSSION

In a first step, chemical shifts of methyl (C-β) and methylene (C-α) carbons are measured for five ethanol concentrations (1M>C>0.05M) in 20 varied non aqueous solvents. The relationships between chemical shifts and concentrations are linear but with very small slopes except for CCl_4, C_5H_{12} and C_7H_{14}. For methyl carbon, an increasing ethanol concentration leads to a shielding effect with solvent 1 to 20 ; a same behaviour is observed for methylene carbon, except for substituted pyridines for which an increasing ethanol concentration leads to a deshielding effect. This behaviour can be attributed to the formation of a strong hydrogen bond between the alcohol hydrogen and electrons of the nitrogen lone pair.

The chemical shifts, extrapolated to infinite dilution, are gathered in tables 1 and 2. It can be noticed that chemical shifts vary on about 1.3 ppm and 2.2 ppm respectively for C-β and C-α ; the lowest values for these two carbons are measured with CH_2I_2, the highest ones are observed with 4-picoline for the methyl carbon and with dichloromethane for the methylene carbon.

TABLE 1

Infinite Dilution Chemical Shifts of Ethanol Carbons

SOLVENT	$\delta_{C-\alpha}$	$\delta_{C-\beta}$
pentane (1)	58.40	18.85
heptane (2)	58.25	18.80
carbon tetrachloride (3)	57.60	18.45
methanedichloride (4)	58.61	18.70
1,2-dichloro ethane (5)	58.31	18.72
1,2-dibromo ethane (6)	57.64	18.55
bromoform (7)	57.26	17.95
chloroform (8)	58.42	18.41
diiodo methane (9)	56.44	17.97
2,2,4-trimethyl pentane (10)	57.85	18.70

TABLE 2

Ethanol-Base Complexes : Observed and Corrected Chemical Shifts

BASE	δ observed		δ corrected	
	C-α	C-β	C-α	C-β
benzene (11)	58.00	18.54	58.58	18.75
mesitylene (12)	58.00	18.62	58.49	18.87
2-F pyridine (13)	57.91	18.98	57.45	18.78
3-Cl pyridine (14)	57.43	19.05	57.26	19.00
pyridine (15)	57.37	19.23	57.11	19.15
4-picoline (16)	17.27	19.32	56.98	19.21
2,4-lutidine (17)	57.00	19.27	56.72	19.16
2,4,6-collidine (18)	56.69	19.15	56.37	19.02
2-OMe pyridine (19)	57.90	18.93	57.64	18.83
2,6-diOMe pyridine (20)	58.21	18.89	57.94	18.79

- Non Specific Medium Effects

Our aim being to characterize the actual effects of hydrogen bonding formation on the ^{13}C shifts in the proton donor molecule, it is mandatory to take into account each mechanism involved in ^{13}C shift variations. In a first time, we have to explicitely evaluate non specific medium effects. For this purpose, according to the previously proposed models of non specific (Van der Waals) solvent effects (10-11), C-α and C-β chemical shifts obtained with solvent 1 to 10 have been plotted (fig. 1 and 2) vs the Rummens solvent function g^2 (10) ($g = (n^2-1)/(2n^2+1)$). Good linear relationships are obtained :

$$\delta C\text{-}\alpha = -39\,g^2 + 59.78 \qquad r = 0.90 \qquad m.d. = 0.23$$

$$\delta C\text{-}\beta = -18\,g^2 + 19.38 \qquad r = 0.92 \qquad m.d. = 0.09$$

The deviation from the correlation line, relative to the methylene carbon, observed for CH_2Cl_2, $CHCl_3$ and $ClCH_2\text{-}CH_2Cl$ can be attributed to the formation of an hydrogen bond between hydrogen of the solvent and alcohol oxygen. A same behaviour has been observed with methanol but not with benzylic alcohol (11) certainly because of its lower basicity ; the elimination of these three points from the regression analysis does not modify significantly the correlation slope. A same deviation is not observed for the relationship regarding the methyl carbon because hydrogen bonding formation effects is much smaller on the C-β carbon. Our experimental procedure (measurements with an internal reference) avoids magnetic susceptibility measurements, but allows only to determine "apparent" medium shifts by respect to Me_4Si.

From the slopes of the preceding δ/g^2 relationships apparent site parameters $S^{i'}$ are deduced : $S^{i'}_{C\text{-}\alpha} = -39$ and $S^{i'}_{C\text{-}\beta} = -18$. Absolute site parameters S^{i} (otherwise attainable via external reference measurements) can be deduced from the TMS sensitivity parameter via the relationship $S^{i} = S^{i'} + S^{i}_{TMS}$ that we recently proposed (12) :

$S^i_{C-\alpha} = -39 + 78 = 39$, $S^i_{C-\beta} = 60$. The sensitivity factor for methyl carbon is close to the values already known (in apolar or weakly polar solutes $67 < S^i < 80$ (13) and for methanol ($S^i = 68$) (8)). For methylene carbon, it differs sligthly from the value obtained for benzylic alcohol ($S^i = 25$) (7), but is in good agreement with the previously determined values for sp_3 methylene carbons ($33 < S^i < 45$) (14).

- Hydrogen Bond Effects

Solvents (11 to 20) can form hydrogen bond with alcohol. Owing to the small variations observed in the chemical shifts, prior to any discussion on hydrogen bond formation, it is necessary to eliminate all other contributions to these chemical shift variations. Magnetic anisotropy corrections have been evaluated from Bovey diagrams (15), using CNDO optimizations to determine the associated complex geometry. For ethanol-pyridine complex, optimized bond lengths and angles (dN...HO = 1.518 A ; dO-H = 1.0549 A ; > O-H...N = 178.99° ; dC-O 1.3727 A ; > COH = 106.9° are similar to those determined for methanol pyridine complex (8) ; so same correction terms are used for the methylene carbon i.e. : -0.3 ppm for planar complex (substituted pyridines, n bases) and 0.48 ppm for out of plane association (benzene and mesitylene, π bases). The correction terms for the methyl group are evaluated assuming for C-C distance the usual value of 1.54 A : - 0.12 ppm for pyridine-ethanol complexes and 0.25 ppm for benzene-ethanol complex. The corrected chemical shifts (table 2) are therefore calculated according to the following equation :

$$\delta_{cor} = \delta_{obs} + S'_i \Delta g^2 + \Delta\delta \text{ anisotropy}$$

$$\Delta g^2 = g^2 \text{ (solvent)} - g^2 \text{ (reference)}$$

$$g^2 \text{ (reference)} = g^2 \text{ (benzene)} = 0.051$$

From table 2, we can observe that increasing solvent basicity induces a deshielding effect on the methyl carbon and a shielding effect on the methylene carbon : from 2-F pyridine to collidine $\delta_{C-\alpha}$ decreases of 1.08 ppm and $\delta_{C-\beta}$ increases of 0.24 ppm only. These variations are attributed to the formation of an hydrogen bonding between hydroxylic hydrogen and base ; the effect is smaller for the CH_3 carbon owing to the transmission factor through the CH_2 group.

We can observe that with 2-OMe and 2,6-diOMe pyridine the chemical shifts are similar to those measured with 2-F pyridine : indeed in these compounds, the methoxy group prevents the approach of the hydroxylic hydrogen and so decreases the hydrogen bond strength.

A good linear relationship between corrected ^{13}C shifts for CH_2 group of ethanol and the corresponding corrected chemical shifts for methanol carbon obtained for the six media common to both studies has been established :

$$\delta_{CH_2} = 1.00\ \delta_{CH_3} + 7.73 \qquad \text{m.d.} = 0.086 \qquad \text{c.c.} = 0.98$$

The slope (unit value) indicates that the sensitivity to hydrogen bond formation of the carbon directly connected to hydroxylic group is the same for CH_3 or CH_2 group, expected since ethanol and methanol have similar acidic character. As a similar behaviour have been shown for CH_2 group sensitivity of benzylic alcohol we can conclude that in aliphatic alcohols the sensitivity of the C-α carbon to H bonding effects is roughly the same. But in contrast, like we have established in previous works (5-6) for phenol-bases complexes, the hydrogen bond formation leads to a deshielding effect of C-1 carbon and these results suggest a different behaviour to hydrogen bond formation between sp^3 and sp^2 carbon directly connected to hydroxylic group. For β carbon our results are similar to those observed with C-1 aromatic carbon of benzylic alcohol complexes ; deshielding effect with H bonded associations (7).

- H Bonding and Electron Reorganisation

Electronic populations localized on each atom of ethanol (free or complexed to pyridine) are calculated at CNDO/2 level. We observed that association induces an important electron reorganization on the hydroxy group : the hydrogen atom loses 502.10^{-4} e and the oxygen atom gains 687.10^{-4} e. The total electron population decreases respectively by 40.10^{-4} and 10.10^{-4} e for C-α and C-β atoms, so only minute variations are observed for the carbon framework. In contrast, for each hydrogen atom of the methylene group the electronic population increases by 143.10^{-4}e and the same is true for the methyl hydrogens (hydrogen in complex plane $\Delta q = 82.10^{-4}$e, out of plane $\Delta q = 51.10^{-4}$e). A same behaviour have been observed for methanol-pyridine complex (8).

The hydrogen bonding effect on C-β chemical shifts (deshielding effect) and on electronic population (charge decrease) are in good agreement with δ-q relationships often quoted in literature especially for sp^2 carbon atoms ; however for C-α carbon a reverse effect is observed (shielding effect when charge decreases). Indeed, it was suggested that, as to C-α carbon, the electron reorganization on neighbouring atoms may have a non negligible influence on ^{13}C shifts. We recently established that the ^{1}H chemical shifts of substituted phenols depend significantly on the electron population on both hydrogen and oxygen atoms (16). Furthermore, Fliszar (17-18) showed that shift-charge correlations can correspond to positive or negative slopes depending upon the hybridation state of resonating nucleus. The invoked reason is that chemical shifts are related to σ and π electron populations with sensitivities differing by size and even sign.

- Differential Behaviour in H_2O and DMSO Solvents

In a last step, we have measured chemical shifts of ethanol carbons in DMSO and H_2O (table 3). For water solvent, values are expressed from

TABLE 3

^{13}C Chemical Shifts of Ethanol in H_2O and DMSO

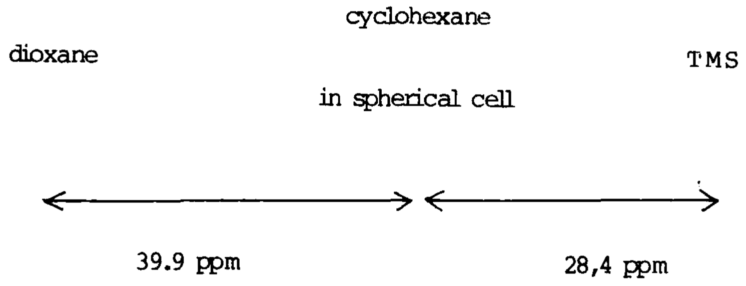
	δ_{H_2O} (a)	(b)	δ_{DMSO} (c)
C-α	- 9.02	59.28	56.10
C-β	- 49.6	18.70	18.50

(a) values from internal dioxane

(b) values from artificial internal TMS

(c) values from internal TMS

internal dioxane reference ; to convert the chemical shift to internal TMS reference, we first determine the chemical shift of dioxane by reference to cyclohexane inserted in a spherical capillary (39.90 ppm) ; secondly, using our previously established relationship (12) between TMS chemical shifts measured from external cyclohexane and the g^2 solvent factor we calculate a chemical shift value of - 28,4 ppm for an artificial TMS in water (by respect to external cyclohexane).



Since we use a spherical cell, it is not necessary to take into account the magnetic susceptibility variations and chemical shifts referenced to TMS are determined in adding 68.3 ppm to experimental values. This value differs slightly from those used in literature (67.4 (19,20) ; 67.86 (21,22) for transforming chemical shifts from internal 1,4-dioxane to chemical shifts from TMS. We can observe table 3 that from DMSO to H_2O the C-α and C-β chemical shift increase respectively by 3.18 and 0.2 ppm. These results are very different of values proposed by Vincendon (3) in a study of ethanol in DMSO-D_2O mixtures ($\Delta\delta$C-α = + 0,5 ppm ; $\Delta\delta$C-β = - 1,75 ppm) for measurements from external reference without taking into account magnetic susceptibility variations and medium effects.

On figure 1 where are reported the chemical shifts variations v.s. the g^2 parameter for C-α carbon, we have set the points corresponding to these two solvents. We observe that the point characterizing ethanol chemical shift in DMSO (56.10 ppm) is far away the correlation line (about 1.8 ppm corresponding to a shielding). For chemical shifts in water, we also notice a deviation from the correlation line (i.e. a deshielding effect of 0.7 ppm). The shielding observed with DMSO can be explained by an hydrogen bond formation between OH group and sulfoxyde oxygen atom. This effect is about twice the deviation measured when acetone is used as solvent (0.8 ppm). In fact, C=O and S=O anisotropy effects are similar as suggested by magnetic susceptibilities values (23), but the S=O group is more basic ($\Delta\nu_{OH}$ $CH_3OD...O=S(CH_3)_2$) = 158 cm^{-1} ; $\Delta\nu_{OH}$ ($CH_3OD...O=C(CH_3)_2$) = 81 cm^{-1}). For water solvent, the deshielding effect can be explained by an hydrogen bond formation between water hydrogen and ethanol oxygen.

For C-β carbon, the chemical shifts in DMSO and water respectively 18.50 and 18.70 ppm are close to the correlation line (δ v.s. g^2) (figure 2) and it the same for acetone solvent (δ_{CH3} = 18.9 ppm). We show that the C-β carbon sensitivity to hydrogen bond forma-

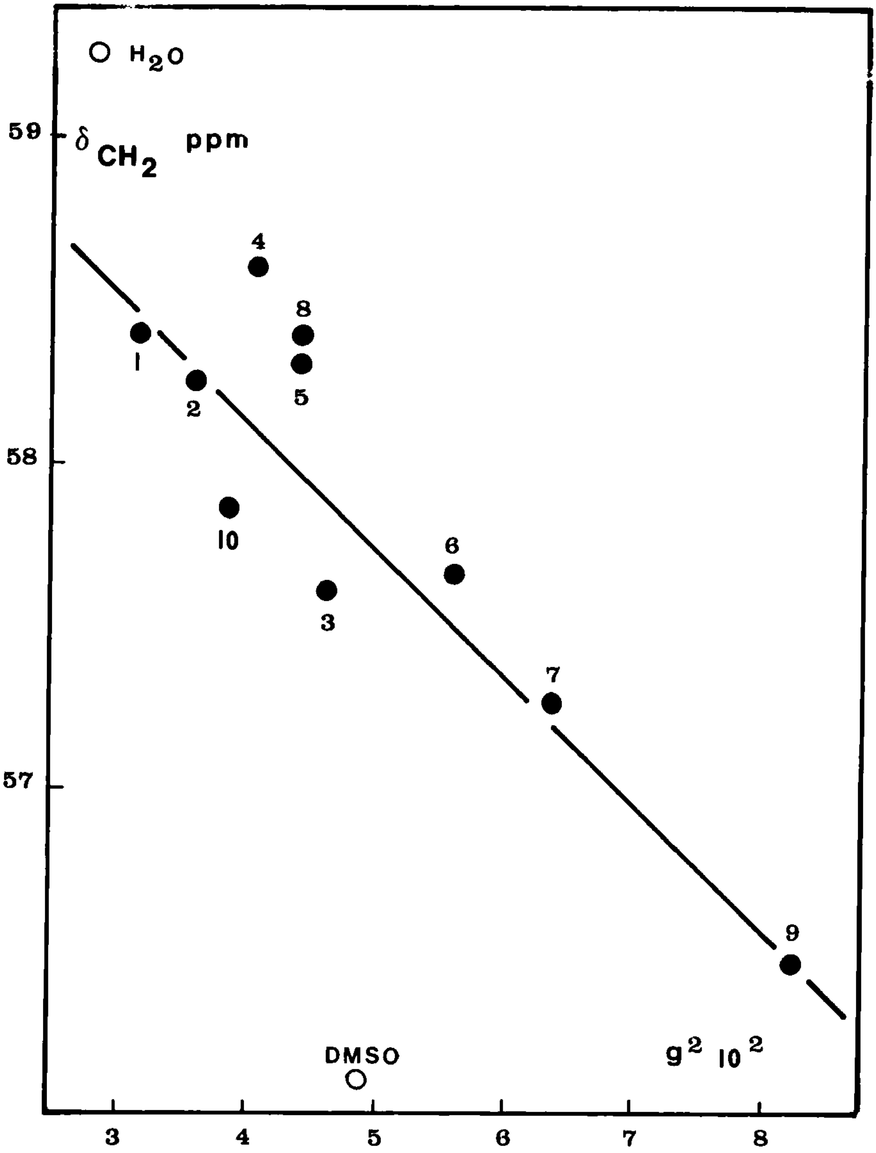


Fig. 1 : Correlation between C-α chemical shifts ethanol and the g^2 factor

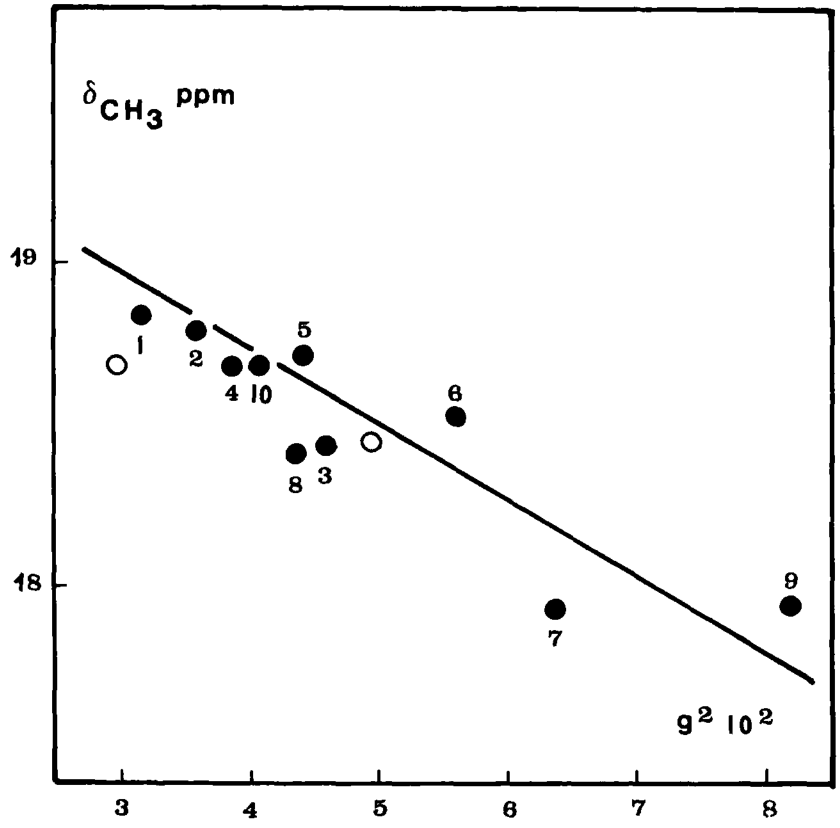


Fig. 2 : Correlation between C-β chemical shifts ethanol and the g^2 factor

tion is very small, contrary to literature results (1-3). The difference observed between our results (high variation on C-α carbon and small variation on C-β carbon) and those of literature (small variation on C-α and great effect on C-β) can be explained by the fact that the literature chemical shifts are measured from external reference and in this case the medium effect from H_2O to DMSO (deshielding effect in internal reference) compensates for the hydrogen bond effect (shielding effect) ; but with C-β carbon the two effects add up.

CONCLUSION

In this work, we characterize the actual effects of hydrogen bonding formation on the ^{13}C shifts in the donor molecule ; we prove that this hydrogen bonding formation leads to a shielding of C-α carbon and have only a small effect on C-β carbon. We are planning now studies of carbohydrates in water and DMSO solvents to determine importance of hydrogen bond for the different hydroxylic groups.

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